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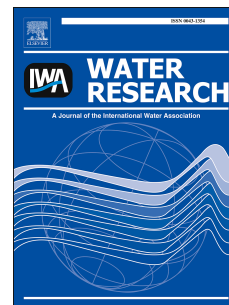
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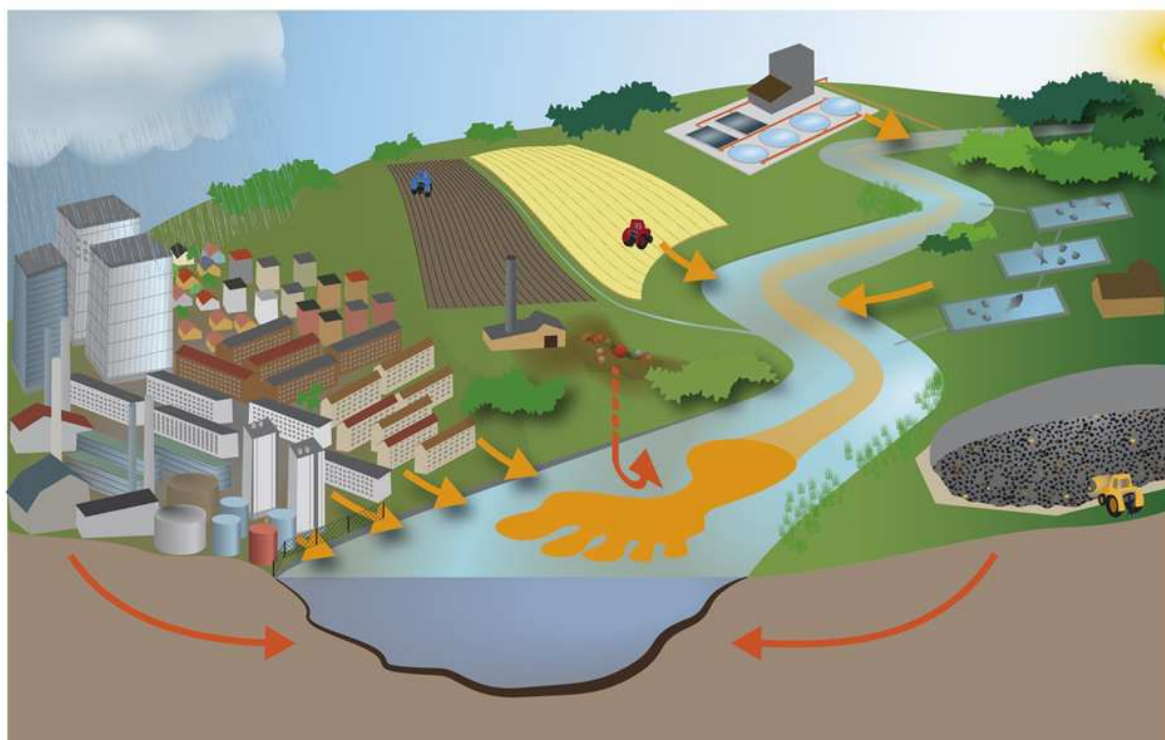
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2 **system**

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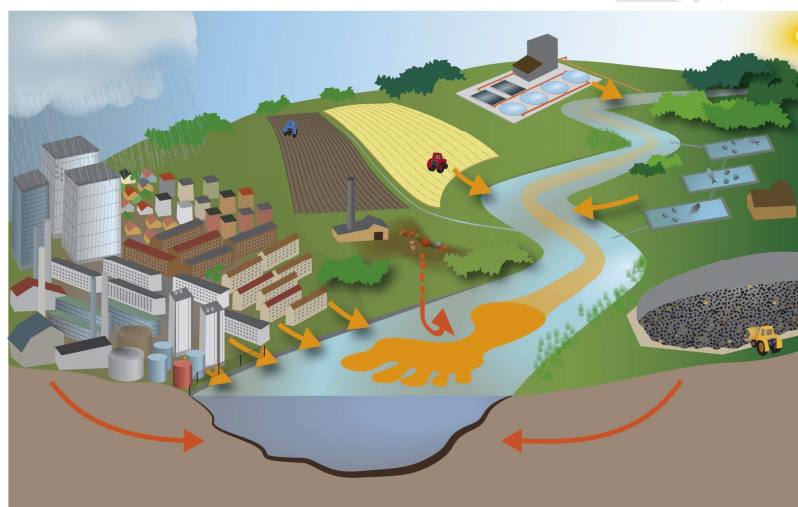
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11 sites; Contaminant mass discharge; In-stream fate; Toxic units



15  
16 **Graphical abstract**

17

## 18 Abstract

19 Traditionally, the monitoring of streams for chemical and ecological status has been limited to  
20 surface water concentrations, where the dominant focus has been on general water quality and the  
21 risk for eutrophication. Mixed land use stream systems, comprising urban areas and agricultural  
22 production, are challenging to assess with multiple chemical stressors impacting stream corridors.  
23 New approaches are urgently needed for identifying relevant sources, pathways and potential  
24 impacts for implementation of suitable source management and remedial measures. We developed a  
25 method for risk assessing chemical stressors in these systems and applied the approach to a 16-km  
26 groundwater-fed stream corridor (Grindsted, Denmark). Three methods were combined: (i) in-  
27 stream contaminant mass discharge for source quantification, (ii) Toxic Units and (iii)  
28 environmental standards. An evaluation of the chemical quality of all three stream compartments –  
29 stream water, hyporheic zone, streambed sediment – made it possible to link chemical stressors to  
30 their respective sources and obtain new knowledge about source composition and origin. Moreover,  
31 toxic unit estimation and comparison to environmental standards revealed the stream water quality  
32 was substantially impaired by both geogenic and diffuse anthropogenic sources of metals along the  
33 entire corridor, while the streambed was less impacted. Quantification of the contaminant mass  
34 discharge originating from a former pharmaceutical factory revealed that several 100 kgs of  
35 chlorinated ethenes and pharmaceutical compounds discharge into the stream every year. The  
36 strongly reduced redox conditions in the plume result in high concentrations of dissolved iron and  
37 additionally release arsenic, generating the complex contaminant mixture found in the narrow  
38 discharge zone. The fingerprint of the plume was observed in the stream several km downgradient,  
39 while nutrients, inorganics and pesticides played a minor role for the stream health. The results  
40 emphasize future investigations should include multiple compounds and stream compartments, and  
41 highlight the need for holistic approaches when risk assessing these dynamic systems.

42

## 1. Introduction

The increasing modification in land use, land cover and water management driven by urban expansion and increased agricultural production have created multiple chemical stressors impacting surface water bodies on a global scale (Davis et al., 2010; Yu et al., 2014). The impairments are especially noticeable in freshwater stream systems, which are highly connected to their landscape via their draining systems (Fausch et al., 2010). The growing understanding of the complexity inherent in mixed land use stream systems (Ding et al., 2016 Stutter et al., 2007) has shifted the focus towards risk assessment approaches at the catchment scale, as opposed to controlling isolated contamination events. It is still a major challenge in practice however, to quantify relevant sources, pathways and chemical stressors impacting stream water for use in determining essential source management and remedial measures.

Determining the chemical status of a stream is relatively straight-forward from a legislative perspective, as it has been defined in part by a set of (European) environmental quality standards (EQS) for priority substances in the stream water (EQS Directive (2008/105/EC)), and in part by legislation derived within the individual Member State countries (e.g. Danish EPA, 2010). In reality, however, determining where to collect suitable field data for comparison with EQS values is complicated, especially in these systems. Specifically, the high temporal and spatial variations of the contamination dynamics create a complex picture where the distribution of contaminants will depend on a number of factors (e.g. hydrological system, physico-chemical properties, biogeochemical processes) leading to diverse impacts within different stream compartments, i.e. stream water, hyporheic zone or bed sediments. The transport, fate and toxicity of contaminants in such systems are thus a challenge to assess, so despite intensive research spanning decades (Schwarzenbach et al., 2006; Kuzmanovic et al., 2016), approaches for conducting proper risk assessments in such environments are still being sought after.

The contaminant mass discharge (CMD) approach seems promising for the quantification of anthropogenic point source-related pollutants, such as contaminated sites (Newell et al., 2011) or wastewater outlets into streams. It can be used to support an overall evaluation of the magnitude and importance of these various sources. Furthermore, measurements of the contaminants in stream

71 water can be used to quantify CMD from a source, as shown by Aisopou et al. (2015). However,  
72 this approach cannot take changes due to attenuation and transformation processes in e.g. the  
73 hyporheic zone into account, potentially leading to underestimations. It is also more limited for  
74 contaminants with a higher tendency to sorb, as the concentrations often will be very low in stream  
75 water.

76 It is not possible to make similar mass discharge estimations for diffuse sources such as trace  
77 elements or metals coming from anthropogenic and geogenic sources. Here, the source function is  
78 related to the geological settings and often worsened by acidification or changes in the prevailing  
79 redox conditions (Edmunds et al., 1992; Cozzarelli et al., 2016). The understanding and distinction  
80 between anthropogenic and geogenic sources of metals thus requires insight of the governing  
81 biogeochemical processes in the groundwater, hyporheic zone and stream, while the geogenic  
82 source is often inaccessible for remedial actions.

83 Toxic units (TU) is a commonly used screening tool providing an initial overview of the potential  
84 ecological risk, where dissolved-phase chemical concentrations are used as a proxy for  
85 environmental effects based on the use of toxicity values (Rasmussen et al., 2015, Tomlin, 2001).  
86 Application of this tool makes it possible to assess the water quality in the stream water (SW),  
87 hyporheic zone (HZ) and bed sediment (BS) calculated as pore water (PW). Notably, laboratory-  
88 derived toxicity tests cannot reproduce the complexity of the receiving environment, nor can they  
89 provide insight on the long-term impact of continuous low-dose contamination (Beketov and Liess,  
90 2012). Nevertheless, it can be used to provide a uniform assessment of all identified chemical  
91 stressors potentially impacting the stream environment, and is thus in line with the requirements of  
92 the European Water Framework Directive (WFD) (EC, 2017).

93 The objectives of this paper are to develop and apply a methodology for holistically assessing the  
94 quality of a mixed land use stream system at the catchment scale. In order to more accurately assess  
95 the origins and potential toxicity of chemical stressors detected in the various compartments along a  
96 stream corridor, we suggest to combine three approaches: (i) in-stream CMD, (ii) TU and (iii) EQS  
97 for SW, BS (US EPA, 2006), and general water chemistry parameters (DCEE, 2012). The

methodology is applied to Grindsted stream, located in western Denmark. The chemical quality of the SW, HZ and BS was determined, allowing contaminants of concern to be linked to their respective sources. Then for anthropogenic point source-related compounds, their CMD into the stream was estimated, followed by an assessment of the in-stream fate specifically for the organic xenobiotic compounds. Finally, in order to identify key sources and risk drivers, a risk assessment was conducted by combining calculations of predicted ecotoxicity within the CMD framework.

## 2. Material and methods

### 2.1 Grindsted stream study site and potential contaminant sources

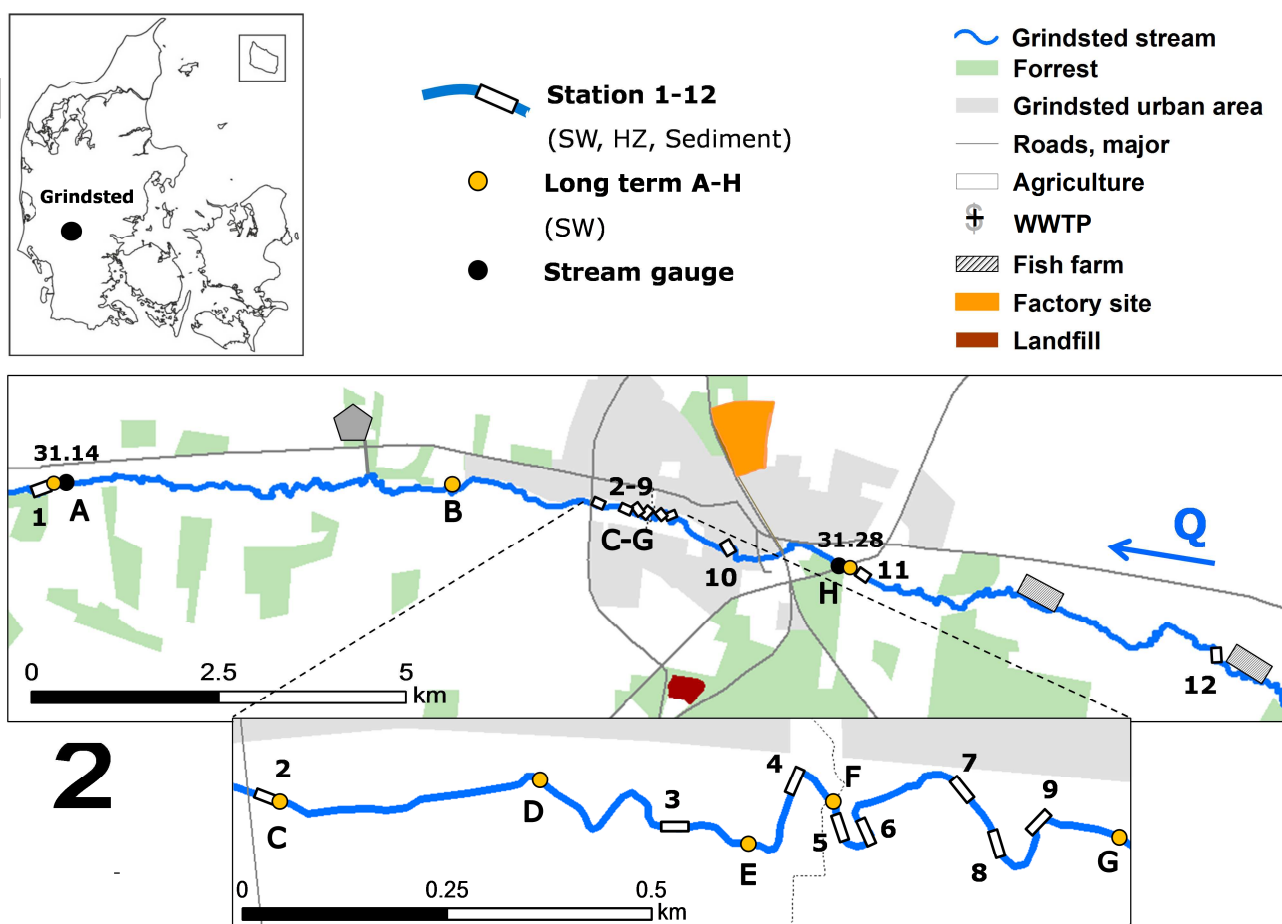
The study site comprises a 16-km corridor along Grindsted stream with a catchment size of ca. 200 km<sup>2</sup>, representing a typical Danish landscape with diverse land use activities and contaminant sources (Fig. 1). Grindsted stream is generally groundwater-fed with a median flow of 2000 L/s (Nielsen et al., 2014) and is naturally meandering with only few modifications. The stream depth ranges from 1-2.5 m and the width from 8-12 m. The 80 m thick upper aquifer is unconfined and hydrologically connected to the stream. The geology is characterized by Quaternary sand formations (10-15 meter below ground surface, mbgs), underlain by Tertiary sand formations (Heron et al., 1998). Beneath this, a thick and extended clay layer comprises the regional aquitard. Groundwater chemistry of the noncalcareous sandy aquifer indicates that there are increased levels of dissolved trace metals at shallow depths, including aluminum and nickel, due to groundwater acidification (Kjøller et al., 2004).

Potential contaminant sources relevant to the stream include agricultural activities (comprising 54% of the catchment), a wastewater treatment plant (WWTP), two fish farms and diverse urban point and diffuse sources coming from Grindsted – a town with ca. 10,000 inhabitants (12% land use). Grindsted WWTP (Fig. 1) is a potential point source for nutrients and salts to the stream in the lower catchment. In 2014 it discharged 11 and 1.5 tonnes of total-N and total-P, respectively, with an average discharge of 70 L/s to the stream (Billund Vand A/S, 2016). Other industrial discharges (of cooling- and wastewater) come from DuPont factory, with an average of 6 L/s in 2014 containing 316, 0.8 and 0.2 tonnes of chloride, total-N and total-P, respectively (MEF, 2016). The



125 two fish farms, located in the upper catchment, are potential sources for both nutrients and  
126 pharmaceuticals (DANMAP, 2005).

127 Moreover, two large-scale contaminated sites are located within 2 km of the stream: a  
128 pharmaceutical factory (in operation from 1914-1999), and an unlined, abandoned municipal  
129 landfill that closed in 1977 (Kjeldsen et al., 1998). Previous studies have shown that the  
130 groundwater beneath and downstream of both sites are contaminated by multiple chemicals,  
131 including pharmaceuticals (e.g. sulfonamides, barbiturates) and petroleum hydrocarbons (benzene,  
132 toluene, ethylbenzene, m-/p-/o-xylenes, i.e. BTEX) (Kjeldsen et al., 1998; Holm et al., 1995; Rügge  
133 et al., 1995). The groundwater plume from the factory site also contains high concentrations of  
134 chlorinated ethenes: tetrachloroethylene (PCE) and trichloroethylene (TCE), and their degradation  
135 products cis-1,2-dichloroethylene (cis-DCE) and vinyl chloride (VC) (Hunkeler et al., 2011). The  
136 contaminant groundwater plume has been delineated from the factory site and the flow is towards  
137 the stream (Rasmussen et al., 2016; Balbarini et al., 2017). The local and regional flow direction of  
138 the landfill plume is not well understood, and it is unclear whether it enters the stream. In addition  
139 to these and other smaller-scale contaminated sites located along the stream corridor, other urban  
140 sources consist of storm water runoff, traffic (incl. road salt for deicing purposes) and biocide  
141 applications (weed control; paint) in residential and public areas.



**Fig. 1: Land use distribution along the investigated stream corridor, including Grindsted factory, Grindsted landfill, WWTP, and the two fish farms (note the sizes are magnified). The stream flow direction, Q, is illustrated with a blue arrow. The two online monitoring stream gauges, 31.28 and 31.14, are shown with black dots. Locations are also shown for the (i) twelve sampling stations, investigated in Apr 2014 (open rectangles labelled 1-12), and the (ii) eight long-term stations, monitored from Aug 2012 to Mar 2015 (yellow circles, labelled A-H).**

## 2.2 Investigation strategy

In order to assess and link probable chemical impacts to their respective sources in the catchment, samples were taken from the SW, HZ (40-60 cm depth) and BS. Twelve sampling stations (1-12) were strategically placed in Apr 2014 (Fig. 1). Selected stations were re-visited in Aug 2014 (i.e. 2, 4, 6, 8, 10). The density and number of sampling stations were higher in the central part of the stream corridor, where urban sources and inflow of contaminated groundwater from the factory site were expected. Particular attention was given to compounds measured in previous surveys of the stream and in plume constituents from the factory and landfill sites (Rasmussen et al., 2016; Holm et al., 1995; Rügge et al., 1995).

## 2.3 Sampling and analytes

In Apr 2014, one SW sample was taken in the middle of the stream, in the middle of the water column at each of the twelve stations. Water samples from the HZ were collected at stations 4, 6

161 and 8 in the middle of the stream. Sampling of the upper 5 cm of the BS was conducted at all  
162 stations. 36 subsamples were taken evenly distributed across each station and subsequently pooled  
163 into one sample. In Aug 2014, the 5 selected stations were then re-investigated, focusing on a  
164 smaller area of the initial 50 m station, i.e. 5 x 5 m<sup>2</sup>. Note that at station 4, two sub-stations were  
165 placed: one in the upstream part of the station (4US) and one downstream (4DS). SW, HZ and BS  
166 samples were collected at all stations.

167 SW and HZ samples were analyzed for general water chemistry, selected trace metals and a  
168 range of xenobiotic organic compounds (Table S1). The BS was analyzed for total organic carbon  
169 (TOC), selected trace metals, pesticides and associated metabolites (Table S1). Furthermore, the  
170 grain size distribution was determined. Hydrophilic chlorinated ethenes, BTEX and naphthalene  
171 (BTEX,N) and the pharmaceutical compounds were omitted from the BS analysis, as they were  
172 expected to be below detection limits (Table S2).

#### 173 *2.4 Monitoring of stream flow and long-term water quality*

174 Seasonal variation of the stream flow (Q) from summer 2012 to spring 2015 was quantified by  
175 daily monitoring of the stream water level (h) at the two gauging stations (31.28, 31.14; Figures 1,  
176 S1). To establish a Q-h relationship, 26 independent manual measurements of h and Q were  
177 executed at both stream gauges. Additional stream flow measurements were used to describe the  
178 variation along the investigated stream corridor (Nielsen et al., 2014; Rasmussen et al., 2016)  
179 including manual measurements at five stations in this study (1, 2, 4, 9, 11; Table S3).

180 Seven sampling campaigns were carried out to investigate seasonal variations in SW quality (Aug  
181 2012, Apr, May, June, Aug and Oct 2014, Mar 2015) and support the analysis of the in-stream  
182 contaminant fate at the eight long-term sampling points (A-H, Fig. 1). Chlorinated ethenes and  
183 BTEX,N were included in all seven sampling campaigns, while the pharmaceutical compounds  
184 were included in three campaigns (Aug 2012, Apr and Aug 2014). In Oct 2014 and Mar 2015,  
185 ethene and ethane were included; compound-specific stable carbon isotope analyses of cis-DCE and  
186 VC were conducted in Oct 2014.

187

190 General water chemistry parameters were measured at all sampling sites (Tables S4-5). Field  
191 measurements of pH, electrical conductivity (EC) and dissolved oxygen were conducted by  
192 electrodes (WTW Multi 3420). Biological oxygen demand (BOD, ortho-phosphate and ammonium-  
193 N in SW were analysed following the European Standard methods (DS/EN 1899-1999, DS/EN  
194 1189-1997, DS 11732-2005, respectively). Total-N and total-P were measured using the Kjeldahl-N  
195 method and Danish standard DS-291. The samples to be analyzed for inorganic anions (chloride,  
196 bromide, dissolved nitrate-N, sulphate-S) were filtered (0.45  $\mu\text{m}$ ) and stored on dry ice in the field  
197 until analysis. The samples were analyzed using ion chromatography, Dionex ICS-1500, with an  
198 Ion Pac AS 14A mm Column (P/N 056904) and Ion Pac AG14 "Guard" Column in combination  
199 with an anion suppressor, Metrohm 833 IC. Samples to be analyzed for NVOC were filtered (0.45  
200  $\mu\text{m}$ ) and preserved with 4M phosphoric acid (17 w/w% to pH 2) and analyzed by oxidation with  
201 catalytic combustion (TOC 5000A, Shimadzu, ASI-5000 autosampler).

#### 202 2.5.2 Xenobiotic compounds and metals in water samples

203 Samples for the analysis of chlorinated ethenes and degradation products, and BTEX,N were  
204 analyzed following the procedure according to McKnight et al. (2012; Tables S6-7). Compound-  
205 specific stable carbon isotope analysis for chlorinated ethenes was done according to Hunkeler et al.  
206 (2011). Analyses of pesticides and associated metabolites (Tables S8-9), as well as pharmaceutical  
207 compounds (e.g. sulfonamides, barbiturates; Tables S6-7) were conducted by ALS Denmark A/S.  
208 Samples for the analysis of metals were filtered (0.2  $\mu\text{m}$ ) and preserved with 1% v/v nitric acid in  
209 the field and analyzed using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-  
210 OES, MPX Vista Axial, Auto sampler SPS3; Tables S10-11).

#### 211 2.5.3 Sediment analysis

212 TOC was measured by initially homogenizing and acidifying the BS sample with phosphoric  
213 acid ( $\text{H}_3\text{PO}_4$ ) before it was analyzed on a LECO Induction Furnace CS-200. The grain size  
214 distribution was determined according to Heron et al. (1998; Tables S12-13). Metal concentrations,

except mercury, were determined according to US EPA standard 3051A, and analyzed using ICP-OES. Mercury was measured by ALS Denmark A/S. Pesticide and associated metabolite concentrations were determined by the Swedish University of Agriculture (Jansson and Krueger, 2010).

## 2.6 Data analysis methods

### 2.6.1 Calculation of in-stream contaminant mass discharge and dilution factors

Using a simple mass balance and plug flow interpretation to describe the mixing and transport of a discharged compound to a stream, an estimate of the CMD can be derived (for details see Aisopou et al., 2015):

$$CMD = C_{mix} \cdot Q_{mix} \quad (1)$$

where  $CMD$  is the total mass discharge of the compound at the point of fully mixed conditions in the stream,  $C_{mix}$  is the SW concentration at the point of fully mixed conditions and  $Q_{mix}$  the flow of the stream at the mixing point.

A linear approach following the course of the stream was employed to estimate the stream flow,  $Q$ , at a given point between the two stream gauges. A comparison of the stream flow at the two points showed a maximum variation of only 7.5% over time (for details see Table S14).

A dilution factor for stream stretches of interest was furthermore calculated using manual flow measurements (Table S3). These were estimated using the most upstream measurement as a reference (dilution equals 1.0) for downstream reach calculations. The estimated factors were employed to determine the degree of dilution for organic xenobiotic compounds in the SW.

### 2.6.2 Calculation of predicted ecotoxicity

The toxicological potential for dissolved-phase contaminants was estimated using the TU approach, with *Daphnia magna* as the benchmark organism following Tomlin (2001):  $TU = C_i / LC50_i$ , where  $C_i$  is the measured concentration of compound  $i$ , and  $LC50_i$  is the corresponding acute 48-h 50% mortality value for *D. magna* exposed to compound  $i$  (Table S1). The TU for all detected compounds was estimated for the SW, HZ and BS compartments. Based on the linear dilution approach, the HZ concentrations for stations 1, 2, 3, 5, 7, 9, 10 and 12 in Apr 2014 were assumed to

242 be equal to SW concentrations if no increment was observed in the downstream SW. Estimations of  
243 BS toxicity for sediment-bound compounds were calculated by converting measured bulk sediment  
244 concentrations to PW according to equilibrium-partitioning theory (Di Toro et al., 1991; van der  
245 Kooij et al., 1991; Tables S12-13).

246 We calculated the sum of all TUs for each compartment ( $\Sigma$ TU, Table 2), for each of five detected  
247 compound groups (defined as: chlorinated ethenes, BTEX,N, metals, pesticides, pharmaceuticals),  
248 which is in line with the principle of screening-level risk assessments. The more conservative TU  
249 threshold value,  $TU \geq -3.0$ , was used for determining impact levels associated with acute observed  
250 effects on macroinvertebrate communities in the field (Liess et al., 2008).

### 251 3. Results and discussion

#### 252 3.1 Connecting spatial contaminant discharges to sources

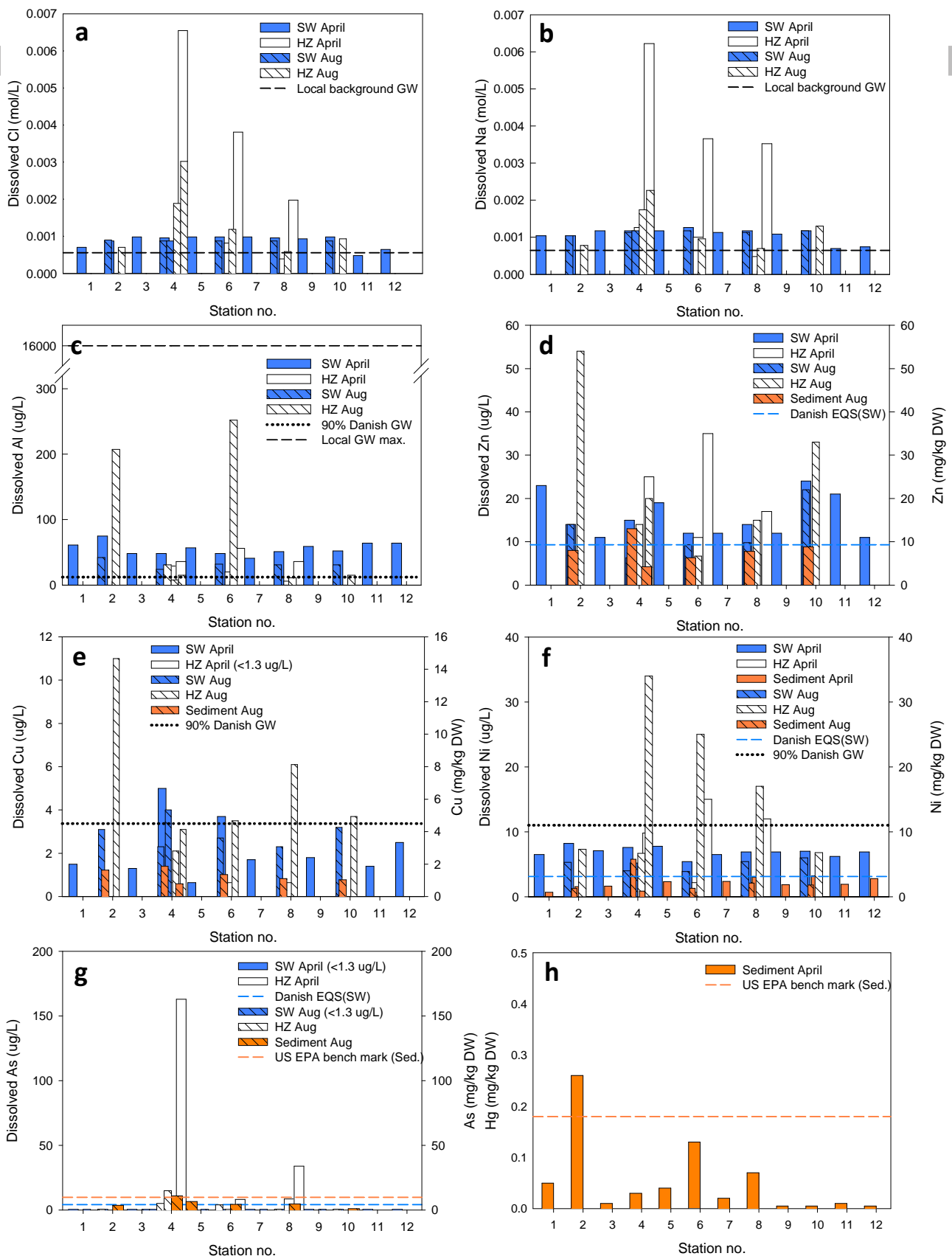
##### 253 3.1.1 Stream flow, general water quality and nutrients

254 The stream flow monitored between June 2012 and Mar 2015 varied from 1500-4100 L/s at the  
255 central gauge 31.28 (Fig. 1), with an average increase of 855 L/s to the downstream gauge 31.14  
256 (Fig. 1, Fig. S1). The oxygen level and biological oxygen demand (BOD) in the SW were equally  
257 stable throughout the stream corridor with values above 9 mg O<sub>2</sub>/L and below 1.4 mg BOD/L (see  
258 Tables S4-5 for general SW quality parameters). Surprisingly, only a small nitrogen-enrichment and  
259 no phosphorous influence were observed in the SW despite that agriculture is the main land use in  
260 the catchment. The nitrogen input from the WWTP was also minor, contributing only 6% to the  
261 total nitrogen increase along the entire stretch (Figure 1) (Table S15). Although nutrients are  
262 viewed as key components for SW quality, their importance for Grindsted stream is minor and will  
263 not be discussed further.

##### 264 3.2.2 Macro-ions

265 A significant increase of chloride, sodium and EC was observed in the urban upstream SW  
266 (between stations 11 and 10) in Apr 2014 (Fig. 2 A-B, Table S4). A similar pattern was detected in  
267 Aug 2014 and in previous studies (Table S5; Rasmussen et al., 2016; Petersen, 2012), while the

268 cations calcium, magnesium and potassium seemed stable. A calculation of the chloride input  
269 coming from industrial discharges (316 tonnes/yr) compared to the estimated increase at station 10  
270 of 1,192 tonnes/yr showed that it was only responsible for 24% of the chloride increment (Fig. 1,  
271 Tables 1, S15). This particular 1.5 km stream stretch drains an area where three larger roads cross or  
272 run close to the watercourse, indicating road salting for deicing purposes as a potential source as  
273 reported in other studies (Cooper et al., 2014). The consistently high salt content at station 10 in  
274 both Apr and Aug (and in previous campaigns) suggests groundwater as the main pathway, rather  
275 than seasonal run-off to the stream during winter.



**Fig. 2: Spatial occurrence of (a-b) macro-ions: Cl, Na (shown in molar concentration), and (c-g) trace metals: Al, As, Cu, Ni and Zn in SW, HZ and the upper 5 cm of the BS. The sediment content is shown for (h) Hg. Note the sub-scale can differ from subfigure to subfigure. The local background level of Cl and Na are shown for groundwater beneath farmland in the area according to Nielsen et al. (1998), and Al beneath grassland by Kj  ller et al. (2004). The Danish Cu EQS(freshwater) ranges from 1-12  $\mu\text{g/L}$  (Table 2). The US EPA benchmark (sediment) values of Cu, Ni and Zn are respectively 31.6 mg Cu/kg DW, 460 mg Ni/kg DW and 121 mg Zn/kg DW, well above the detected concentrations and are therefore not included.**



284  
285  
286

**Table 1: Point and diffuse sources identified along Grindsted stream coming from anthropogenic and geogenic origins, including specific chemical stressors, estimated CMD, expected pathway to the stream and presumed duration for the discharge. Estimations are based on the SW concentrations measured in Apr 2014 (Tables S4, S6, S15-16).**

	Chemical compounds	CMD	Pathway to stream	Source nature
<b>Anthropogenic point sources:</b>				
Industrial discharge	Chloride	316 kg Cl/yr	Stream water discharge	Continuous source
Urban activities (road salting)	Sodium chloride	1,192 kg Cl/yr 728 kg Na/yr	Groundwater discharge	Continuous source
Contaminated site (Factory site, 1. entry)	Chlorinated ethenes, benzene, pharmaceuticals	212 kg VC/yr 49 kg benzene/yr 101 kg sulfanilamide/yr	Groundwater discharge	Continuous source
Contaminated site (Factory site, 2. entry)	Pharmaceuticals	44 kg sulfanilamide/yr 31 kg VC/yr 19 kg benzene/yr	Groundwater discharge	Continuous source
Fish farms	Pharmaceuticals (sulfonamides)	8.9 kg sulfathiazole/yr	Stream water discharge	Presumable a variable source
<b>Anthropogenic diffuse sources:</b>				
Agricultural activities (manure)	Copper, nickel, zinc	-	Groundwater discharge	Continuous source
(manure, fertilizer)	Nitrogen	-	Atmospheric deposition, surface water run-off	Continuous source with periodic peaks due to stormflow events
(crop protection spraying)	Pesticides	-	Groundwater discharge and surface water run-off	Continuous with periodic peaks in the discharge due to seasonal spraying
Urban activities	Pesticides	-	Groundwater discharge	Continuous source
Urban activities/traffic emission	Toluene	-	Atmospheric Deposition	Continuous source
<b>Geogenic diffuse source:</b>				
A natural release of trace metals	Barium, copper, nickel, zinc	-	Groundwater discharge	Continuous source
Acidification of the non-calcareous aquifer	Aluminum, copper, nickel, zinc	-	Groundwater discharge	Continuous source
<b>Geogenic point source:</b>				
Groundwater plume	Arsenic, nickel	-	Groundwater discharge	Continuous source

287

### 288 3.2.3 Metals

289 The dissolved iron (Fe) concentration in SW (Tables S4-5) was found to comply with the Danish  
 290 ‘moderate standard’ for streams (>0.2 to 0.5 mg/L; DCEE, 2012). The stable but elevated level  
 291 throughout the stream corridor could be due to the local geochemistry of the upper aquifer, which  
 292 has a naturally high content of Fe (DCEE, 2012). The overall pattern indicated that the HZ was  
 293 more reduced in the urban stations, comprised of the upstream area of station 4, and stations 6 and 8  
 294 (Tables S4-5; and previous studies: Rasmussen et al., 2016; Petersen, 2012). These areas are

295 characterized by low nitrate and high dissolved Fe and manganese (Mn) concentrations, indicating  
 296 Fe-reducing conditions in the HZ (Christensen et al., 2000).

297 Dissolved barium (Ba), copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn) in SW all exceeded the  
 298 Danish EQS in both campaigns (Apr and Aug 2014; Table 2, Tables S10-11) and the detected  
 299 concentrations in the HZ were frequently even higher. The SW concentrations of Ba, Cu, Ni and Zn  
 300 were, however, within the values typical for Danish groundwater (90% quantile, Table 2) indicating  
 301 the stream is groundwater-fed.

302 The combination of elevated aluminum (Al), Cu, Ni and Zn concentrations (Table 2) could  
 303 further indicate an acidification of the aquifer, as reported in a catchment study by Kjøller et al.  
 304 (2004). They observed specifically an increased release of Al and Ni; yet, Cu and Zn can also  
 305 potentially be mobilized via acidification as reported by Edmund et al. (1992). Another potential  
 306 source for the increased Cu and Zn concentrations in SW could be from the application of pig  
 307 manure to agricultural fields, similar to the findings of Gräber et al. (2005) and Formentini et al.  
 308 (2015). This is a growing source of concern in many countries, as it is used as a replacement for  
 309 antibiotics and as growth promoters at pig farms (Gräber et al., 2005; Jondreville et al., 2003).

310 **Table 2: Detected levels for the dissolved trace metals in Grindsted SW in 2014, Danish streams and groundwater in 2004-**  
 311 **2012, as well as Danish EQS values for freshwater where relevant. All concentrations are in µg/L. Dashes indicate data is not**  
 312 **available.**

Dissolved trace metals	Grindsted SW		Danish SW <sup>1</sup>		Reference SW Skjern stream		Danish groundwater <sup>1</sup>		Danish EQS (freshwater) <sup>2</sup>
	Median	90 % <sup>3</sup>	Median	90 % <sup>3</sup>	Median	90 % <sup>3</sup>	Median	90 % <sup>3</sup>	
Aluminum	48	64	0.79	1.5	-	-	2.20	12	-
Arsenic	< 1.3		0.73	2	-	-	0.54	3.40	4.3
Barium	75	80	63	82	-	-	71	200	9.3 + 15 (natural background level)
Cadmium	< 1.3		-	-	0.034	0.040	0.011	0.16	≤0.08-0.25
Copper	2.3	4.3	1.1	2.5	0.95	1.5	0.41	4.50	1 (12 upper level)
Chrome	< 1.3		0.30	0.61	-	-	0.34	0.88	Cr(VI) 3.4, Cr(III) 4.9
Lead	1.8	3.7	0.23	0.63	0.08	0.69	0.03	0.075	0.34
Nickel	6.5	7.7	1.3	2.0	3.35	3.7	1.10	11	2.3 + 0.82 (natural background level)
Vanadium	< 1.3		0.48	0.92	-	-	-	-	4.1
Zinc	14	22	4.2	14	8.9	18	3.10	41	7.8+ 1.5 (natural background level)
Mercury	<0.2		<0.001	0.0039	0.003-0.018 (n=2)		<0.001	0.010	0.05

313 <sup>1</sup> DCEE, 2015, median values from 2004-2012

314 <sup>2</sup> Danish EPA, 2010

315 <sup>3</sup> 90% quantile

316  
 317 The level of dissolved arsenic (As) in the stream was always below the Danish EQS. However,  
 318 compared to typical Danish groundwater values, a notably high level for both As and Ni was

319 observed in the HZ within the urban area (90% quantile: Table 2, S10-11). This coincided with the  
320 stations where strongly reduced conditions were detected. The Fe-reduction process may, in  
321 addition to the dissolution of Fe(II), mobilize trace metals. It therefore indicates a secondary effect  
322 of the prevailing redox conditions and may be the main explanation for an increased geogenic  
323 release of As in the discharge area of the contaminant plume. Observations of arsenic in  
324 groundwater at the streambank further confirm elevated As in the core of the contaminant plume  
325 (data not shown). Similarly, Cozzarelli et al. (2016) reported increased As levels under strongly  
326 reduced conditions in a petroleum hydrocarbon plume.

327 In contrast, the mobility of Ni is not known to be affected by the redox conditions, but a  
328 relationship was observed between increased Ni concentrations and increased NVOC (Tables S4,  
329 S10-11), as also seen in landfill leachate-polluted groundwater by Christensen et al. (1996). The  
330 presence of dissolved humic acids has been shown to promote Ni solubility through complex  
331 formation, thereby removing the dissolved ions from the state of equilibrium with the sediment  
332 particle. This suggests geogenic processes related to the strongly reduced and carbon-rich factory  
333 plume as being responsible for the increased levels of As and Ni.

334 It should be noted that the metal content in the BS was very low compared to freshwater  
335 sediment benchmarks (US EPA, 2006) for chronic exposure using non-lethal endpoints for sensitive  
336 invertebrate species (Tables S12-13). Metals in BS were thus considered insignificant and not  
337 considered further.

### 338 3.2.5 Chlorinated ethenes, BTEX, N and pharmaceuticals

339 High concentrations of cis-DCE and VC (2289 - 4498 µg/L) were detected in the HZ, covering a  
340 50 m stretch, which was followed by an abrupt increase in SW concentration (from 0.4 to 6.4 µg  
341 VC/L) that remained elevated far downstream (Fig. 3A-D). This strongly implies the main pathway  
342 for this contamination to enter the stream occurs via groundwater discharge. The recurring temporal  
343 pattern observed in the stream also indicates that the contaminant plume discharge is a significant  
344 and continuous source. A similar appearance in the stream was observed for the pharmaceutical  
345 compounds, e.g. sulfamethiazole and meprobamate (Fig. 3E-H). However, they were detected over

346 a longer distance in the HZ (ca. 0.5 km) in lower concentrations and in a more scattered spatial  
347 pattern at stations 4, 6 and 8, which made the peak for SW less distinct. Based on the known  
348 fingerprint of the factory plume, stations 4-8 thus comprise the main location for chemical input via  
349 groundwater to the stream.

350 Benzene showed a pattern comparable to the degradation products of the chlorinated ethenes,  
351 while toluene was detected in similar concentrations in both the SW and HZ (Tables S6-7)  
352 throughout the stream corridor. The recurring pattern and constant level of toluene in the SW  
353 suggests a diffuse source, e.g. atmospheric deposition from traffic emissions/urban activities in the  
354 area, as also observed by Kenner et al. (2014).

355 The CMD estimated at the point of fully mixed conditions, i.e. at station 3, are shown in Table 1  
356 and S16 (1. entry). A small additional input of chlorinated ethenes, benzene and pharmaceuticals  
357 was observed between stations 3 and 2 in the stream (Tables 1, S6). This input had a different  
358 contaminant composition (Table S16, 2. entry) with a noticeable decrease in the discharge of  
359 chlorinated ethenes compared to benzene and the pharmaceuticals. Here, the source could be a  
360 plume originating from another part of the rather large factory site (Fig. 1).

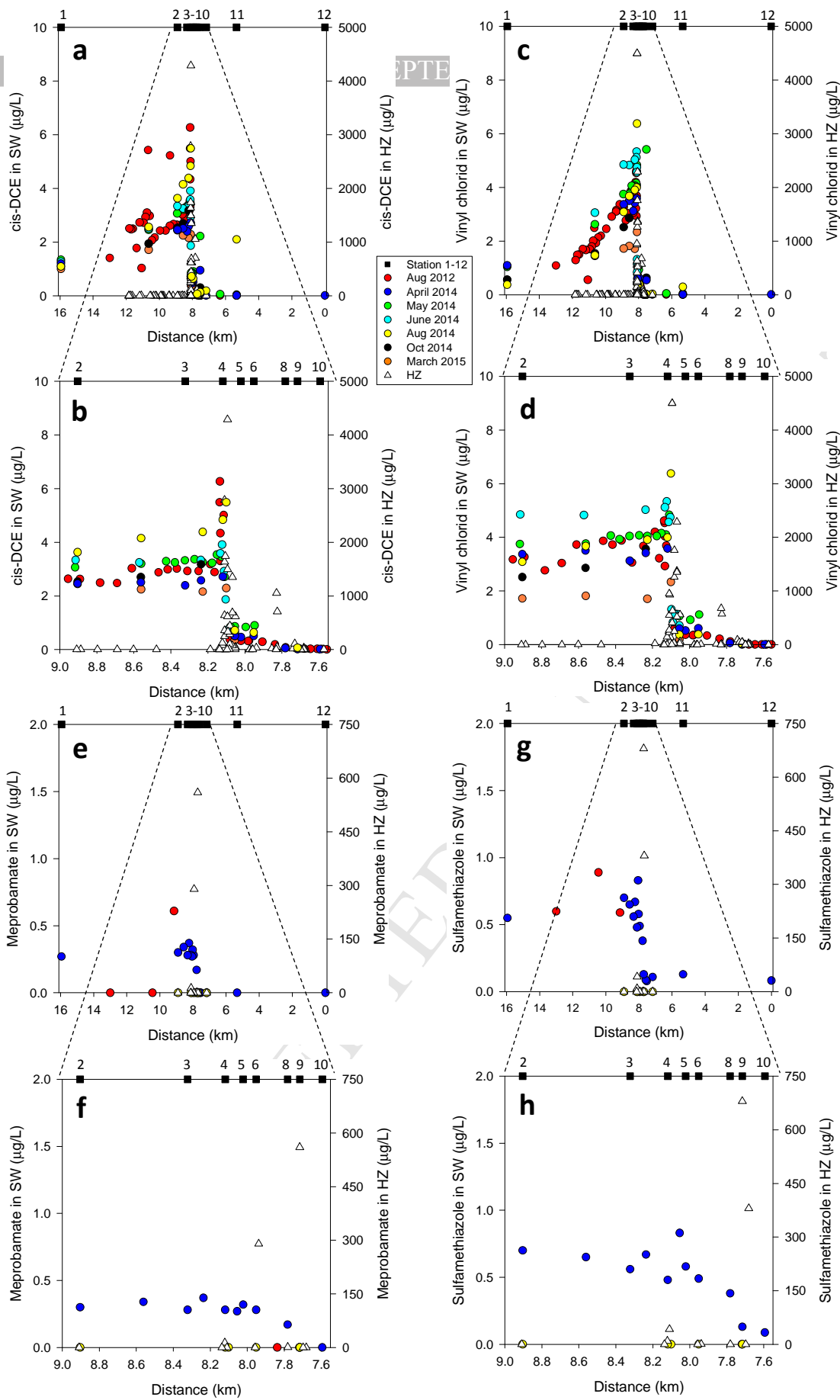


Fig. 3: The long term monitoring results for SW and HZ are shown for two chlorinated ethene metabolites, cis-DCE (a-b) and VC (c-d), and the pharmaceutical compounds meprobamate (e-f) and sulfamethiazole (g-h) for the period of Aug 2012 to Mar 2015. The locations of the twelve sampling stations (1-12) are presented at the top of the graphs. Note the scale can differ from figure to figure.

Pharmaceutical compounds frequently used in aquaculture were also identified downstream of both fish farms (Fig. 1). Sulfamethiazole was detected at station 12, just downstream of the 1<sup>st</sup> fish farm, whereas sulfathiazole and sulfadiazine were additionally detected at station 11, just downstream of the 2<sup>nd</sup> fish farm. Assuming fully mixed conditions at the two stations downstream of the fish farms, a small but significant contribution could be estimated (Tables 1, S16). The composition of this source can be distinguished from the factory plume via the composition of the sulfonamides. In the upper catchment where the fish farms are located, sulfamethiazole, sulfathiazole and sulfadiazine were present in equal amounts, while sulfamethiazole dominated the pharmaceutical input from the groundwater plume (Table S16). However, evaluating the stream corridor as a whole, it can be seen that most of the pharmaceutical contamination originates from the factory plume, leaving the input from the fish farms as only minor (Tables 1, S16).

The importance of dilution, degradation and volatilization on the in-stream fate of the groundwater-borne organic contaminants was examined from a point of fully mixed conditions (at station 3), to 7 km downstream from the mixing point (at station 1) (Fig. 1). The reduction in contaminant concentrations showed that, e.g. cis-DCE, VC and benzene were on average 63% lower than would be predicted due to dilution alone (Table S17), whereas the reduction in sulfonamide concentrations (sulfanilamide, sulfaguanidine, sulfamethazine) could be explained by dilution only (Table S17). The highly volatile compounds cis-DCE, VC and benzene can potentially be removed by volatilization and degradation. However, degradation is not likely due to the short retention time (< 20 hr) in addition to the stable molar ratio of the chlorinated ethenes detected in the SW, and constant stable carbon isotope fractionation throughout the stream stretch (Tables S18-19). Thus, the chlorinated ethenes and benzene concentrations are most likely attenuated predominantly by dilution and volatilization.

#### 3.2.4 Pesticides

Pesticides were in general found in very low concentrations (Tables S8-9) along the stream corridor. Two metabolites of commonly used agricultural pesticides, 4-nitrophenol (a component used in various fungicides and insecticides) and aminomethylphosphonic acid (AMPA, a metabolite of glyphosate, a widely used herbicide in both urban and agricultural settings; McKnight et al., 2015), were found only in the SW but at most stations, indicating they mainly originate from diffuse sources. 2,6-dichlorobenzamide (BAM, a metabolite of the herbicide dichlobenil, banned since 1997), however, was detected in both the HZ and SW at stations 4 and 8, which suggests an input via groundwater discharge from the previous use of dichlobenil in urban areas. Additional herbicides and insecticides (e.g. 4-chloro-2-methylphenol, metamitron, 2,6-dichlorophenol, dimethoate) were only detected in the HZ of the urban area. The presence of pesticides in the upper BS showed a similar pattern (Tables S12-13). The low concentrations detected in all three stream compartments indicates a minor impact overall coming from pesticides at the time of the two campaigns.

#### **4. Risk assessment, sources and contaminant mass discharge**

In order to estimate the effects of the various chemical compounds present in Grindsted stream, TU was calculated for the detected compounds and  $\Sigma$ TU for the identified compound groups (Table 2). Overall the results revealed that the metals posed the highest predicted ecotoxic risk to the investigated stream corridor in both the SW and HZ compartments, while contaminants originating from groundwater plume(s) may be acting as an additional stress factor in the HZ in particular between stations 4 and 8.

This interpretation is based on the predicted toxicological potential ( $\log \Sigma$ TU) for the trace metals detected in both the SW and HZ, where it showed remarkably high values ranging from -1.78 to 0.37 (Table 2). This was mainly driven by the Al and Cu concentrations at all stations, while As, Ni and Zn also contributed to the elevated levels in the HZ. The  $\log \Sigma$ TU values in both compartments indicate a substantial potential toxic risk throughout the stream corridor (Table 2), according to both Liess et al. (2008, given threshold:  $\log \Sigma$ TU  $\geq$  -3) and von der Ohe et al. (2004, threshold:  $\log \Sigma$ TU  $\geq$  -2). The diffuse geogenic sources of metals were therefore found to play a substantial role for the



stream quality. Similar findings were also observed in rivers at the urban fringe across Northern America (Naik and Hammerschmidt, 2011). Moreover, metals from geogenic sources were likely to be enhanced locally due to the reduced conditions within the contaminant plume, leading to the increased mobilization of dissolved Fe and Mn.

Table 2: log $\Sigma$ TU for metals, pesticides, chlorinated ethenes, BTEX, and pharmaceuticals detected in the three compartments (SW, HZ, PW(BS)) of Grindsted stream in Apr and Aug 2014. The log $\Sigma$ TU for a compartment is only shown when at least one value exceeded -3.0 at a station along the stream (see Tables S6-S13 for more details). Note that the total sum for log $\Sigma$ TU presents the sum of all five compound groups. The compound groups responsible for the dominant (potential) ecotoxic risk at each of the sampling stations are highlighted in bold. “<DL” indicates that all compounds in the group were below the detection limits.

Apr	St.1	St.2	St.3	St.4	St.5	St.6	St.7	St.8	St.9	St.10	St.11	St.12
Metals												
SW	-0.92	-0.97	-1.02	-0.72	-1.03	-0.81	-1.00	-1.17	-0.92	-1.12	-0.92	-0.85
HZ	-0.92	-1.04	-1.02	-1.45 to -1.02	-1.10	-1.52 to -0.84	-1.00	-1.78 to -1.17	-0.92	-1.12	-0.92	-0.85
Pesticides												
PW(BS) <sup>a</sup>	<DL	<DL	-3.63	-4.54	-4.16	<DL	-2.38	-2.86	-3.98	<DL	<DL	<DL
Chlorinated ethenes												
HZ	-4.59	-4.10	-4.13	-2.47 to -1.96	-4.25	-4.23 to -3.16	-4.25	-3.43 to -3.14	-4.47	<DL	<DL	<DL
BTEX												
HZ	-3.88	-3.61	-3.83	-3.76 to -1.70	-3.92	-3.41 to -2.80	-3.98	-4.15 to -2.98	-4.07	-4.15	-4.27	-2.81
Pharmaceuticals												
HZ	-2.52	-2.49	-2.53	-0.64	-2.48	0.47	-2.76	0.76	-5.22	-4.99	-4.91	-5.04
Total sum of logΣTU												
SW	-0.91	-0.95	-1.00	-0.71	-1.01	-0.80	-0.99	-1.17	-0.92	-1.12	-0.92	-0.85
HZ	-0.91	-1.02	-1.01	-0.58 to 0.45	-1.08	0.47	-0.99	0.77	-0.92	-1.12	-0.92	-0.85
Aug	St.2		St. 4DS	St. 4US		St.6		St.8		St.10		
Metals												
SW	-0.87		-1.04	-0.83		-0.95		-0.99		-0.88		
HZ	-0.29		-1.09	-0.84		-0.45		-0.72		-0.86		
Chlorinated ethenes												
HZ	-6.12		-3.51	-1.24		-3.60		-4.42		-5.46		
Pharmaceuticals												
HZ	<DL		-2.61	-0.48		-4.61		-3.14		-3.38		
Total sum of logΣTU												
SW	-0.87		-1.04	-0.83		-0.95		-0.99		-0.87		
HZ	-0.29		-1.08	-0.27		-0.45		-0.72		-0.86		

<sup>a</sup> PW(BS) is the pore water calculated based on the be sediment concentrations.

The presence of the groundwater-borne organic contaminant groups (chlorinated ethenes, BTEX, pharmaceuticals) only showed significant potential toxicity in the HZ at stations 4, 6 and 8 in Apr (Table 2), whereas in Aug it was reduced to only the smaller area of station 4 (4US). This risk was found to be quite spatially limited, e.g. impact zones were localized over very short distances. Nonetheless, once they enter the SW, the elevated levels of contaminants were found to persist more than 7 km downstream of the primary discharge zones and in the case of VC (a known human



carcinogen), these concentrations were well above the Danish EQS (0.05 µg VC/L). Moreover, a recent study has documented sub-lethal effects of VC on *D. magna* (10-d chronic exposure tests) at the gene, cellular and life-history levels at concentrations down to 0.1 µg VC/L (Houde et al., 2015). The potential impacts in the SW could thus extend over much greater distances compared to the risk in the HZ.

The input from the fish farms and presence of toluene in SW, on the other hand, did not show any potential risk to the stream system. The detected pesticides also posed no risk (-3.65 to -6.14) in either campaign, except for the BS(PW) at the two urban stations 7 and 8 (-2.38 and -2.86, respectively). This toxicity was driven by the presence of the hexachlorocyclohexane isomers (alfa, beta, delta).

The high input of chloride (app. 1,200 kg Cl/yr) leading to stable levels in the stream (25-35 mg Cl/L) throughout the investigated corridor were still well below the EQS value stated by the European EPA (120 mg Cl/L; Danish EPA, 2013). Even the highest concentrations, detected in the HZ (232 mg Cl/L), were far below acute toxicity levels documented to affect benthic invertebrates in freshwater streams similar to Grindsted (3,172-4,154 mg Cl/L; Elphick et al., 2011). The input was therefore not considered to pose a risk to the stream.

The application of a combination of in-stream CMD, threshold values (EQS) and TU to assess the chemical quality of SW, HZ and BS seems promising. We identified the sources of the contamination and were in many cases also able to quantify the actual CMD. The geogenic origin of metals and the associated risk suggests that metals should be considered in the risk assessment of streams in particular for mixed land use systems. Surprisingly pesticides were of less importance, while the significant impact of xenobiotic compounds from the factory plume was striking. CMD in the range of several 100 kg/yr for chlorinated ethenes and pharmaceutical compounds impacting the stream for several kilometers deserves attention and is valuable information for the focus of future remedial actions.

## 460 5. Perspectives

461 Traditionally, the monitoring of streams has been focused on SW concentrations as debated in  
462 Fairbairn et al. (2015) and much focus has been on the general water quality and the risk for  
463 eutrophication (McKnight et al., 2012). We consider if the actual risk for such systems has been  
464 underestimated, particularly if the identification of the actual risk drivers was based on a narrow,  
465 single compound group approach (e.g. nutrients, BOD) looking only into the impact of one or two  
466 stream compartments. Taking Grindsted stream as an example, the general water quality, nutrients  
467 and oxygen demand are all indicative of a healthy stream, while the actual results, including metals  
468 and organic xenobiotic compounds, show the opposite. Thus, we recommend a much broader focus  
469 including heavy metals and organic xenobiotics in multiple compartments in future monitoring  
470 programs.

471 Fortunately, many recent studies address multiple stream compartments (Kim and Carlson, 2006;  
472 Beketov et al., 2013) or multiple compounds (Gerner et al., 2017; Yu et al., 2014). However, it  
473 seems that only a few studies included geogenic sources, HZ and the groundwater pathway in their  
474 investigations (Naik and Hammerschmidt, 2011; Roy and Bickerton, 2012; McKnight et al., 2015).  
475 The groundwater pathway and geogenic sources require special attention for metals, where  
476 mobilization of Fe and As in strongly reduced contaminant plumes, release due to acidification, or  
477 increased mobility of Ni in carbon-rich environments may add additional complexity.

478 Investigations in mixed land use systems have also been reported including multiple contaminants  
479 and compartments (e.g. Fairbairn et al., 2015; Nazeer et al., 2014), but often the link to actual  
480 sources is missing (e.g. Kuzmanovic et al., 2016; Castro-Catalá et al., 2016). Our findings suggest  
481 that it is advisable in future studies to address mixed land use systems holistically including the  
482 CMD approach. The quantification of CMD from stream concentrations is very useful for an initial  
483 ranking of the identified sources and will be able to guide future remedial actions for contaminated  
484 sites. This will be crucial for the management of the stream at the catchment scale using e.g. river  
485 basin management plans in order to fulfill the requirements of the WFD and in general to improve  
486 the chemical quality in streams.

## 6. Conclusion

This study aimed to assess chemical stream quality in mixed land use systems by combining the evaluation of the chemical quality and predicted toxicity potential for the three stream compartments (SW, HZ, BS) using the CMD framework, the latter particularly to quantify the potential impact from the identified anthropogenic point sources in catchments. The method developed in this study was tested and yielded promising results at a 16-km stream corridor of the Grindsted stream (Denmark).

The groundwater-fed stream was substantially impaired by both geogenic and anthropogenic sources of metals throughout the investigated stream corridor, reaching critical toxic potential levels in both the SW and HZ compartments. Notably, the impairment was quite uniformly distributed, which made the impact of additional chemical stressors especially in the HZ more pronounced. The inflow of a contaminated groundwater plume gave an unexpectedly manifold impact to the chemical quality, particularly in the HZ. We suggest that the highly localized “toxic potential risk zones” were additionally impacted by the strongly reduced water – characterized by high concentrations of Fe – created by the degradation of xenobiotic compounds, leading additionally to the release of arsenic.

The methodology applied in this study is thus capable of providing a holistic picture of the chemical quality in a stream, which includes the ability to integrate stressor interactions not ordinarily evaluated together (i.e. organic and inorganic contaminants). Moreover, it points to the compartments that may represent a potential hazard to the stream ecosystem, and gives an indication of the gravity of the situation. We think that the method will be suitable for many mixed land use systems, and that the complexity of the chemical stressors will be misleadingly evaluated (i.e. underestimated) if only a single compound group or compartment are covered.

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**Highlights**

- A methodology to determine multiple stressor impact has been developed for streams
- Risk assessment of organic and inorganic chemicals in mixed land use systems
- Integrated evaluation of stream water, hyporheic zone and bed sediment is proposed
- A contaminant mass discharge framework can identify key sources and risk drivers
- Contaminated sites with substantial plumes may pose a risk to stream water quality